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(54) **Preparation of high activity silica-supported hydrotreating catalysts and catalysts thus prepared.**

(57) **Process for preparing silica-supported catalysts containing 10-25 %w molybdenum and from 1-5 %w nickel and/or cobalt as hydrogenation metals, wherein a dried silica support is impregnated with an aqueous solution or an aqueous mixture obtained by contacting a hydrogenation metal compound with a nitrogen-containing organic ligand such as ethylene-diamine, tetraacetic acid, diethylene triamine or nitrilotriacetic acid, in the presence of water.**

**EP 0 181 035 A2**

PREPARATION OF HIGH ACTIVITY SILICA-SUPPORTED  
HYDROTREATING CATALYSTS AND CATALYSTS THUS PREPARED

The present invention relates to improvements in the preparation of silica supported hydrotreating catalyst via aqueous methods. Silica-supported hydrotreating catalysts, when prepared by conventional aqueous pore-filling impregnation with catalytically active metals, tend to have very poor activity compared to corresponding alumina-based catalysts. This is thought to be because the metal oxides ( $\text{MoO}_3$ ,  $\text{NiO}$ ,  $\text{CoO}$ ) interact very weakly with the support, and thus are very poorly dispersed on the support.

Potentially, silica-based hydrotreating catalysts should perform well in treating residual oil feedstocks. Silica-based catalysts should be less prone to coke formation than alumina-based catalysts because of the lower acidity of silica. Since coke deposition is a major catalyst deactivator in such applications, an active and stable silica-based catalyst could have an enormous impact on hydrotreating such feedstocks.

Processes for hydrogenating olefins and aromatics in the presence of catalysts comprising molybdenum and nickel in a particular atomic ratio supported on silica are known from U.S. patent specifications 3,167,496 and 3,167,497. These catalysts are prepared by conventional aqueous impregnation, preferably with the precursor of the molybdenum catalytic agent prior to impregnation with the precursor of the nickel catalytic agent. The molybdenum compound content ranges between 12 and 35 %w (as  $\text{MoO}_3$ ), based on total weight of the catalyst. The nickel compound is preferably present in an amount to provide an atomic ratio of molybdenum to nickel between about 2-3.

In U.S. patent specification 3,420,771 a process is disclosed for hydrotreating an asphaltenic hydrocarbonaceous charge stock containing either sulphurous or nitrogenous compounds in contact with a catalyst prepared by impregnating hydrated silica which has

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not been calcined (containing 5-15 %w water) with from 4-30 %w of aqueous molybdenum compounds prior to calcining. Preferably the catalyst also contains from about 1-6 %w nickel. Nickel nitrate hexahydrate and phosphomolybdic acid are suggested as the source of catalytically active metals.

These prior art methods of preparing silica-supported catalysts all suffer from the disadvantage of poor catalytic metals distribution on the support. It has now been found that silica-based hydrotreating catalysts which overcome this disadvantage by having an improved dispersion of metals on the support, thereby greatly increasing catalyst activity, can be prepared via an aqueous method when use is made of certain large nitrogen-containing organic compounds.

The present invention thus relates to a process for preparing silica-supported catalysts containing 10-25 %w molybdenum and from 1-5 %w nickel and/or cobalt as hydrogenation metals, which comprises impregnating a dried silica support with an aqueous solution or an aqueous mixture obtained by contacting a hydrogenation metal compound with a nitrogen-containing organic ligand in the presence of water.

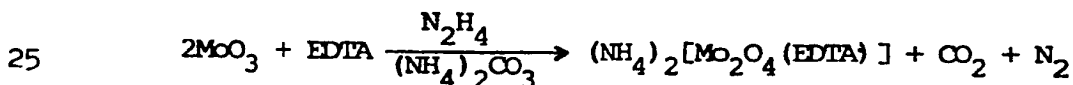
Without wishing to be bound to any particular theory, it would appear that the catalysts according to the present invention are prepared by methods which are believed to have in common that they shut off the formation of three-dimensional oxide lattices that sulphide to large crystallites. The approach presented herein involves the coordination of large, nitrogen-containing organic ligands to an  $\text{MoO}_x$  fragment, thereby preventing them from packing into the  $\text{MoO}_3$  lattice. Examples of suitable nitrogen-containing organic ligands comprise ethylenediamine tetraacetic acid (EDTA), diethylene triamine (DT), nitrilotriacetic acid (NTA), derivatives thereof and related compounds.

When EDTA is used as large nitrogen-containing organic ligand the process according to the present invention is suitably carried out by:-

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- (a) preparing a slurry of about equal quantities of  $\text{MoO}_3$  and EDTA in water to provide from 10 to 25 %w of Mo on said support;
- (b) adding from at least said equal quantity up to about a double quantity of  $(\text{NH}_4)_2\text{CO}_3$  to the slurry and mixing same;
- 5 (c) adding about half as much hydrazine to the mixture as the quantity of  $(\text{NH}_4)_2\text{CO}_3$  added;
- (d) heating the mixture from step (c) to a temperature sufficient to form  $(\text{NH}_4)_2[\text{Mo}_2\text{O}_4(\text{EDTA})]$  in a reasonable time;
- 10 (e) impregnating a dried silica support with the solution from step (d) at elevated temperature;
- (f) drying the Mo-impregnated silica at elevated temperature;
- (g) impregnating a dried silica support with a desired quantity of aqueous nickel and/or cobalt salt solution either before or after step (e); and
- 15 (h) drying the Ni and/or Co impregnated silica at elevated temperature.

Methods for preparing molybdenum compounds used to prepare the improved catalysts according to the invention have been reported by R.C. Pecsock and D.T. Sawyer in J. Am. Chem. Soc., 79, 5496 (1956) and by D.T. Sawyer and J.M. McKinnie in J. Am. Chem. Soc., 82 4191 (1960). However, a much more tractable synthesis was devised for the method of the invention as follows:



The compound was prepared in situ in >95% yield and impregnated directly on the carrier. In addition to  $\text{MoO}_3$ , suitable  $\text{MoO}_x$  compounds include the molybdates, e.g.,  $\text{MoO}_4^{=}$ ,  $\text{Mo}_2\text{O}_7^{=}$  and  $\text{Mo}_7\text{O}_{24}^{-6}$ .

30 An interesting feature of the preparative system described hereinabove is the observation of severe deactivation of the catalyst if heated above 200 °C in either  $\text{N}_2$  or  $\text{O}_2$  before sulphiding. At 400 °C more than half of the activity has disappeared. The deactivation observed may well correspond to thermal ( $\text{N}_2$ ) or oxidative ( $\text{O}_2$ ) ligand degradation followed by

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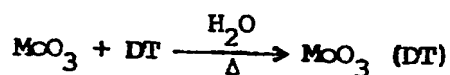
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sintering of the resultant metal oxide fragments. The X-ray diffraction patterns of the sulphided form of the active and deactivated catalyst were consistent with this explanation, with crystalline  $\text{MoS}_2$  being present in the deactivated catalyst, but not in the active version.

When DT is used as large nitrogen-containing organic ligand the process according to the present invention is suitably carried out by:-

- (a) preparing a slurry of an amount of  $\text{MoO}_3$  and diethylene triamine in water to provide from 10 to 25 %w Mo on said support;
- (b) heating and mixing the slurry in sufficient water to dissolve the  $\text{MoO}_3$ ;
- (c) impregnating a dried silica support with the solution from step (b) at elevated temperature;
- (d) drying the Mo-impregnated silica at elevated temperature;
- (e) impregnating a dried silica support with a desired quantity of aqueous nickel and/or cobalt salt solution, either before or after step (c); and
- (f) drying the Ni-Mo or Co-Mo impregnated silica at elevated temperature.

A suitable method for preparing the molybdenum compound used in this particular embodiment of the process according to the invention has been reported by W.F. Marzluff, Inorg. Chem., 3, 395 (1964). The compound may be prepared in situ by the reaction shown below and impregnated directly on the carrier.



In addition to  $\text{MoO}_3$ , suitable  $\text{MoO}_x$  compounds include the molybdates, e.g.,  $\text{MoO}_4^{=}$ ,  $\text{Mo}_2\text{O}_7^{=}$  and  $\text{Mo}_7\text{O}_{24}^{-6}$ . X-ray diffraction patterns and Raman spectra of a sulphided catalyst prepared in accordance with the invention were consistent with the dispersion/activity explanation presented hereinabove.

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When NTA is used as large, nitrogen-containing organic ligand the process according to the present invention is suitably carried out by:-

- (a) dissolving an appropriate amount of nitrilotriacetic acid in ammonium hydroxide;
- (b) adding to the mixture from step (a) an amount of  $\text{MoO}_x$  to provide from 10 to 25 %w Mo on said support;
- (c) heating the mixture in step (b) until the reaction is substantially complete;
- (d) cooling the mixture from step (c) and adding an amount of nickel and/or cobalt salt to provide from 1-5 %w Ni and/or Co on said support;
- (e) impregnating a dried silica support with the aqueous mixture from step (d);
- (f) drying the Ni-Mo and/or Co-Mo impregnated silica at elevated temperature.

A suitable method for preparing the molybdenum compound used in this particular embodiment of the process according to the invention is as follows:-



Dispersion control was achieved by a general method whereby a capping ligand was used on  $\text{MoO}_3$  to control sterically the crystallinity of  $\text{MoO}_3$ . Further limitations on Mo particle size was attempted by chelation of nickel on the edges of some of the  $\text{NTA} \cdot \text{MoO}_3^{-3}$  units, thereby interrupting the  $\text{MoO}_x$  lattice.

The above compound was prepared in situ and impregnated directly on the carrier. In addition to  $\text{MoO}_3$ , suitable  $\text{MoO}_x$  compounds include the molybdates, e.g.,  $\text{MoO}_4^{=}$ ,  $\text{Mo}_2\text{O}_7^{=}$  and  $\text{Mo}_7\text{O}_{24}^{-6}$ .

Suitable hydrotreating catalysts in accordance with the invention generally contain from 10-25 %w molybdenum and from 1-5 %w nickel and/or cobalt on a dried silica support. Preferably, the catalysts will contain from 10-20% molybdenum and from 2-4 %w

nickel and/or cobalt. Of the latter metals, nickel is the most preferred.

The Ni and/or Co compounds included in the catalysts according to the invention may be incorporated either before or after the Mo compound is impregnated therein when use is made of EDTA or DT as the organic nitrogen compound. Prior art methods for incorporating these metals are well known and are not critical to the performance of the catalysts of the invention. A suitable method for incorporating nickel is given in Example 1.

The activity testing of the catalysts according to the present invention was done in microreactor systems. These units are of conventional, fixed-bed, downflow design. Each unit consists of a 127 mm O.D. reactor with a preheat section, a phase separator and a large product tank. Unit pressure is controlled by a motor valve on the outlet gas line and inlet  $H_2$  rate is maintained by pressure drop across a length of capillary tubing. LAPP pumps are used for charging liquid feed. Emergency circuitry automatically shuts down the unit in the event of fire, high reactor temperature, high or low unit pressure or loss of instrument air.

A standard catalytically-cracked heavy gas oil was used as the microreactor test feed (feed properties: 88.99% C; 9.68%  $H_2$ ; 1.28% S and 482 ppmW). The test conditions used were as follows: 58.7 bar, 340-370 °C, 1.0-2.0 LHSV, 2-4  $H_2$ /oil mol ratio.

Catalysts were crushed, screened to 0.3-1 mm and dried at 482 °C for testing. To facilitate control of the reactor temperature the catalysts were diluted 1-1 by volume with a high-density alumina or silicon carbide ground to 0.3-1 mm. Prior to processing hydrocarbon feed, the catalysts were presulphided at atmospheric pressure with 5%  $H_2S$  in  $H_2$ . The temperature program for the presulphiding was 2 hours at 204 °C, 1 hour at 315 °C and 2 hours at 371 °C. Depending upon the metals content, the catalysts will contain from 10-20 %w sulphur.

In a typical Ni/Mo or Co/Mo hydrotreating catalyst preparation method catalytically active metals are deposited on a support by a dry (pore volume) impregnation technique. In this method, the

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support is impregnated with a quantity of metal-salt solution that is just sufficient to be absorbed in the pore volume of the support. The impregnating solution is generally prepared in two parts initially. One part contains the molybdenum salt and most of the water that can be used. After most of the molybdenum salt has dissolved (with heating and stirring),  $H_2O_2$  (30%) is added (about 0.4 ml/g of Mo) to aid solubilization. The other part of the solution contains the Ni and/or Co salt(s) and sufficient phosphoric acid (85%) to aid the solubility and stability of the solution and to include about 3 %w P in the catalyst. When both solutions are clear and cool, the Mo solution is added slowly (with vigorous stirring) to the Ni-P or Co-P solution. The combined solution is then diluted to the proper volume and added slowly, usually in one or more steps, to the support. The impregnated catalyst is dried at 121 °C for about 2 hours and then calcined in air at 482 °C for about 2 hours.

A substantial increase in the hydrodenitrification (HDN) activity, relative to existing commercial catalysts, is required to commercialize a new hydrotreating catalyst. In an effort to develop such an improved catalyst, a standard 72 hour HDN activity test was used to evaluate the various catalysts. In this test the hydrogenation ( $H_2$ ), HDN and hydrodesulphurization (HDS) activities of a standard catalytically-cracked heavy gas oil were evaluated at 344 °C and 57.8 bar  $H_2$  partial pressure. Activities were compared based on observed rate constants for HDN and on plug flow kinetics for HDS.

Suitable conditions for the hydroconversion processes using improved catalysts according to the invention are as follows: a temperature of 350-420 °C; a total pressure of 75-200 bar; a partial hydrogen pressure of 60-200 bar; a space velocity of 0.4-1.5 kg oil/l catalyst/hour; and a hydrogen feed rate of 250-2500 NL/kg oil feed.

The hydrodenitrification of heavy oil feeds according to the present process is preferably carried out under the following conditions: a temperature of 360-410 °C; a total pressure of



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100-150 bar; a partial hydrogen pressure of 80-150 bar; a space velocity of 0.4-1.0 kg oil/1 catalyst/hour; and a hydrogen feed rate of 500-1500 Nl/kg oil feed.

5 The hydrogen applied can be pure hydrogen or a hydrogen-containing gas, preferably one comprising more than 70% hydrogen. The hydrogen-containing gas may also contain up to about 10% of hydrogen sulphide.

The invention will now be illustrated by the following Examples:

10 EXAMPLE 1

Two catalysts, A (alumina-based) and B (silica-based) were prepared for comparison by a conventional aqueous impregnation method and were not prepared in accordance with the present invention.

15 Catalyst A was a standard commercial hydrotreating catalyst (available from Shell Chemical Company) which was prepared by using a dry (pore volume) metals aqueous impregnation technique to impart metals onto a gamma alumina support. This catalyst was prepared by the typical aqueous impregnation method described herein above. The  
20 composition of this alumina-based catalyst is given in Table 1. The various hydrotreating activities of this catalyst were taken as 1.0 for comparison.

Catalyst B was prepared by impregnating a dried Grade 57 silica (from Davison Chemical, a division of W.R. Grace Co.) with  
25 the same metals solution and dry (pore volume) technique used for Catalyst A. The composition of this silica-based catalyst is also given in Table 1.

A silica-based catalyst, C, was prepared according to the present invention by slurring 14.4 g  $\text{MoO}_3$  and 14.6 g EDTA in 50 ml  
30  $\text{H}_2\text{O}$ . 20 g  $(\text{NH}_4)_2\text{CO}_3$  were then added slowly. Upon completion of this addition, 10 g  $\text{N}_2\text{H}_4$  were added and the mixture was heated at reflux (ca. 90 °C) for 2 hours. The solution volume was then reduced to 38 ml and the mixture was impregnated hot (ca. 90 °C) on 38 g of  
35 Davison 57 silica (0.35-0.85 mm) which had been dried at 400 °C for 2 hours. This material was then dried for 18 hours at 120 °C,

impregnated with 7.2 g  $[\text{Ni}(\text{H}_2\text{O})_6](\text{NO}_3)_2$  in 35 ml  $\text{H}_2\text{O}$ , and dried at 120 °C for 12 hours. The composition of Catalyst C is also given in Table 1.

5 A silica-based catalyst, D, was prepared according to the present invention by slurring 14.4 g  $\text{MoO}_3$  in 25 ml  $\text{H}_2\text{O}$ . To this was added 11 ml diethylene triamine (DT). The volume of this mixture was increased to 50 ml with water and the mixture was heated until all material had dissolved. The solution volume was adjusted to 56 ml with water and the hot solution was used to  
10 impregnate 40 g of 2 mm dia. silica spheres (available commercially from Shell International Chemical Company, Ghent, Belgium) which had been dried at 400 °C for 2 hours. This material was then dried at 120 °C for 12 hours. 8.5 g of  $\text{Ni}(\text{H}_2\text{O})_4(\text{OAc})_2$  (OAc = acetate) was then dissolved in concentrated  $\text{NH}_4\text{OH}$  and diluted to 30 ml with  
15 same.

The dried catalyst precursor was then impregnated with this solution and dried at 120 °C for 12 hours. The composition of Catalyst D is also given in Table 1.

20 A silica-based catalyst, E, was prepared, according to the present invention, by dissolving 19.1 g nitrilotriacetic acid (NTA) in 30 ml 24% ammonium hydroxide. To this was added 14.4 g  $\text{MoO}_3$  and the mixture was brought to boiling. After cooling to 50 °-70 °C, 8.7 g nickel nitrate was added and the mixture was diluted to 50 ml with water. 35 g of 200 °C dried silica spheres were then  
25 impregnated with this mixture and dried overnight at 120 °C. The composition of Catalyst E is also given in Table 1.

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TABLE 1

| Catalyst/<br>(Support)              | Composition<br>(% w) |     | Surface Area<br>m <sup>2</sup> /g |
|-------------------------------------|----------------------|-----|-----------------------------------|
|                                     | Mo                   | Ni  |                                   |
| A (Al <sub>2</sub> O <sub>3</sub> ) | 13.2                 | 2.7 | 160                               |
| B (SiO <sub>2</sub> )               | 15.4                 | 4.6 | 140                               |
| C (SiO <sub>2</sub> )               | 10.6                 | 5.0 | 136                               |
| D (SiO <sub>2</sub> )               | 13.8                 | 2.6 | —                                 |
| E (SiO <sub>2</sub> )               | 15                   | 3   | —                                 |

EXAMPLE 2

The catalysts A-E were heated to about 200 °C, presulphided and compared to determine their relative hydrotreating activities (H<sub>2</sub> = hydrogenation; HDN = hydrodenitrification and HDS = hydrodesulphurization) over the standard catalytically-cracked heavy gas oil having the feed properties described hereinabove. For the tests 10.4 ml of 0.3-1 mm catalyst particles were placed in a microreactor and used to contact the feed at 344 °C, 58.7 bar, H<sub>2</sub>/oil ratio = 4/1 and LHSV = 2.0. Results of the tests are shown in Table 2.

TABLE 2

| Catalyst/<br>(Support) | Relative activity |            |            |
|------------------------|-------------------|------------|------------|
|                        | H <sub>2</sub>    | HDN        | HDS        |
| A                      | 1.00 ± .03        | 1.00 ± .10 | 1.00 ± .10 |
| B                      | 0.48              | 0.20       | 0.27       |
| C                      | 0.92              | 0.93       | 0.78       |
| D                      | 0.75              | 0.77       | 0.46       |
| E                      | 0.95              | 1.12       | 0.88       |

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The relative activity of the commercial alumina-based catalyst A, was taken as 1.00 by definition. As can be seen from Table 2, the activity of the silica-based catalyst B, prepared in the same manner as that normally used for a commercial alumina-based hydrotreating catalyst gave very poor results for all three ( $H_2$ , HDN, HDS) hydrotreating activities. However, the HDN activity of the silica-based catalyst C, prepared according to the invention is within experimental error of the activity of a top quality commercial alumina-based hydrotreating catalyst, A, and nearly five times as active as a conventionally prepared silica-based catalyst. Also catalyst D is nearly four times as active as a conventionally prepared silica-based catalyst.

Catalyst E demonstrated an HDN activity even exceeding that of a top quality commercial alumina-based hydrotreating catalyst A and was nearly six times as active as a conventionally prepared silica-based catalyst. This catalyst E was also within experimental error of the  $H_2$  activity and was only slightly below the HDS activity of the alumina-based catalyst A.

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C L A I M S

1. Process for preparing silica-supported catalysts containing 10-25 %w molybdenum and from 1-5 %w nickel and/or cobalt as hydrogenation metals which comprises impregnating a dried silica support with an aqueous solution or an aqueous mixture obtained by  
5 contacting a hydrogenation metal compound with a nitrogen-containing organic ligand in the presence of water.
2. Process according to claim 1, wherein the dried silica support is impregnated at elevated temperature with the solution from step (d) which has been obtained by:-
  - 10 (a) preparing a slurry of about equal quantities of  $\text{MoO}_3$  and EDTA in water to provide from 10 to 25 %w of Mo on said support;
  - (b) adding from at least said equal quantity up to about a double quantity of  $(\text{NH}_4)_2\text{CO}_3$  to the slurry and mixing same;
  - (c) adding about half as much hydrazine to the mixture as the  
15 quantity of  $(\text{NH}_4)_2\text{CO}_3$  added;
  - (d) heating the mixture from step (c) to a temperature sufficient to form  $(\text{NH}_4)_2[\text{Mo}_2\text{O}_4(\text{EDTA})]$  in a reasonable time; followed by drying the Mo-impregnated silica at elevated temperature; whilst the dried silica support is impregnated with a desired  
20 quantity of aqueous nickel and/or cobalt salt solution either before or after the impregnation with the solution from step (d), and drying the Ni- and/or Co-impregnated silica at elevated temperature.
3. Process according to claim 1, wherein the dried silica support  
25 is impregnated at elevated temperature with the solution from step (b) which has been obtained by:-
  - (a) preparing a slurry of an amount of  $\text{MoO}_3$  and diethylene triamine in water to provide from 10 to 25 %w Mo on said support;
  - 30 (b) heating and mixing the slurry in sufficient water to dissolve the  $\text{MoO}_3$ ;

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followed by drying the Mo-impregnated silica at elevated temperature; whilst the dried silica support is impregnated with a desired quantity of aqueous nickel and/or cobalt salt solution either before or after the impregnation with the solution from step (b), and drying the Ni-Mo or Co-Mo impregnated silica at elevated temperature.

4. Process according to claim 1, wherein the dried silica support is impregnated at elevated temperature with the aqueous mixture from step (d) which has been obtained by:-

(a) dissolving an appropriate amount of nitrilotriacetic acid in ammonium hydroxide;

(b) adding to the mixture from step (a) an amount of  $\text{MoO}_x$  to provide from 10 to 25 %w Mo on said support;

(c) heating the mixture in step (b) until the reaction is substantially complete;

(d) cooling the mixture from step (c) and adding an amount of nickel and/or cobalt salt to provide from about 1-5 %w Ni and/or Co on said support;

and drying the Ni-Mo- and/or Co-Mo-impregnated silica at elevated temperature.

5. Process according to one or more of the preceding claims, wherein the catalyst is heated to about 200 °C and sulphided before being used in a hydrotreating process.

6. Process according to one or more of the preceding claims, wherein the impregnation mixtures contain sufficient catalytically active metals to provide from 10-20 %w molybdenum and about 2-4 %w nickel on said support.

7. Process according to claim 3, wherein the molybdenum impregnation mixture is heated at about reflux temperature of said mixture.

8. Process according to one or more of the preceding claims, wherein the  $\text{MoO}_x$  is  $\text{MoO}_3$ , and the volume of the solution/mixture obtained is adjusted to about the pore volume of the silica support before impregnating same.

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9. Process according to claim 5, wherein the impregnated silica is dried at about 200 °C and sulphided before being used in a hydrotreating process.
10. Process according to any one of the preceding claims, wherein  
5 use is made of silica spheres as support.
11. Process according to any one of the preceding claims, substantially as described herein with particular reference to the Examples.
12. A hydrotreating catalyst comprising from 10-25 %w molybdenum  
10 and from 1-5 %w nickel and/or cobalt as hydrogenation metals supported on silica whenever prepared according to a process as claimed in one or more of the preceding claims.
13. A hydrotreating catalyst comprising from 10-20 %w molybdenum and from 2-4 %w nickel as hydrogenation metals supported on silica,  
15 which catalyst has been prepared by the process according to claim 8.
14. A sulphided hydrotreating catalyst comprising from 10-20 %w molybdenum and from 2-4 %w nickel as hydrogenation metals and from about 10-20 %w sulphur, which catalyst has been prepared by the  
20 process according to claim 5.

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ACTORUM AG

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European Patent  
Office

## EUROPEAN SEARCH REPORT

0181035

Application number

EP 85 20 1771

| DOCUMENTS CONSIDERED TO BE RELEVANT   |   |  |  |
|---|---|--|--|
| Category  | Citation of document with indication, where appropriate, of relevant passages   | Relevant to claim  | CLASSIFICATION OF THE APPLICATION (Int. Cl. 4) |
| Y   | US-A-4 424 141 (GRASSELLI et al.)<br>* Abstract; column 4, lines 38-65; claims 1-10 *   | 1  | B 01 J 23/88<br>C 10 G 45/08                   |
| Y   | US-A-4 005 007 (M.J. O'HARA)<br>* Abstract; column 1, line 38 - column 2, line 2; column 3, line 52 - column 4, line 68; claims 1-7 * | 1  |  |
| A   | GB-A-2 089 803 (HALCON SD GROUP)  |  |  |
| A   | GB-A-1 511 900 (UOP)  |  |  |
| A   | GB-A-1 428 755 (GULF)   |  |  |
| D, A  | US-A-3 167 497 (E. SOLOMON)   |  |  |
| The present search report has been drawn up for all claims  |   |  |  |
| Place of search<br>THE HAGUE  |   | Date of completion of the search<br>18-09-1987   | Examiner<br>LO CONTE C.                        |
| <b>CATEGORY OF CITED DOCUMENTS</b>  |   |  |  |
| X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document |   | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>& : member of the same patent family, corresponding document |  |

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